XPS study of stainless steels in physiological solution containing complexing agent

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In past, orthopaedic implants have been considered as "bioinert" and "biocompatible". Today, careful investigations and sophisticated research techniques have contributed to the increasing recognition that, in long-term, orthopaedic implants may be associated with adverse local and remote tissue responses [1]. These adverse effects are mediated by the degradation products of prosthetic materials, which may be present as particles of wear debris, colloidal organometallic complexes, free metal ions, or inorganic metal salts or oxides [2]. Therefore, the biocompatibility of the materials used to manufacture the orthopaedic implants needs to be re-investigated. The majority of in vitro electrochemical studies have been performed in so-called physiological solution. Human body, however, is not a pure saline environment, and contains different proteins, which are capable of binding metal ions [3]. In the present study the effect of biological proteins is simulated by the complexing agent, i.e., citrate. The study is performed on two different stainless steels differing in Mo content, i.e., orthopaedic stainless steel and commercial AISI 304.

The composition of the passive films was studied using X-ray photoelectron spectroscopy (XPS). In pure physiological solution the film consists of two predominant oxides, i.e., Cr- and Fe-oxides (Fig. 1a,b). Oxides of Ni and Mo are also detected in the film. The strong enrichment of oxidized Cr and Mo in the passive layer, and strong enrichment of Mo and depletion of Fe at the metal surface underneath the passive layer, seem to be responsible for the outstanding corrosion resistance of orthopaedic stainless steel in physiological solution. The addition of citrate significantly affects the composition of the film (Fig. 1c,d). In the lower potential region Fe was strongly depleted. In the higher potential range the enrichment of Mo is smaller than in physiological solution and the depletion of Ni is higher. The addition of citrate affected the composition of the metal surface underneath the passive layer as well. The depletion of Fe, as well as the enrichment of Cr, Mo and Ni is less pronounced.

This study shows that the enhanced dissolution of Fe and Ni by the formation of complexes at the surface of the passive layer leads to a slower passive oxide growth [4].

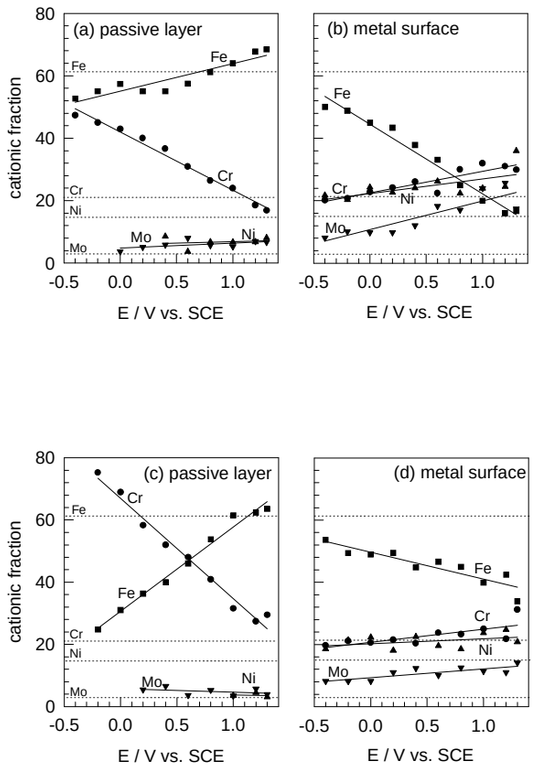

Figure 1: Cationic fractions of the passive layer and the metal surface underneath after oxidation of orthopaedic stainless steel in physiological solution (a,b) and physiological solution containing citrate (c,d) as a function of oxidation potential. Dashed lines denote the bulk values of the atomic fractions for Fe, Cr, Ni and Mo within the alloys. The oxidation time was 300s.

References:

[1] J. Black, in Biological, Material, and Mechanical Considerations of Joint Replacement, B.F. Morrey, Editor, p. 333, Raven Press, New York (1993).
[2] J.J. Jacobs, A.K. Skipor, L.M. Patterson, N.J. Hallab, W.G. Paprosky, J. Black and J.O. Galante, J. Bone Joint Surg., **80-A**, 1447, 1998.
[3] N.J. Hallab, J.J. Jacobs, A. Skipor, J. Black, K. Mikecz and J.O. Galante, J Biomed. Mater. Research, **49**, 353, 2000.
[4] I. Milošev and H.-H. Strehblow, J. Biomed. Mater. Research, **52**, 404, 2000.